PATENT SPECIFICATION

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(54) VINYLIDENE FLUORIDE RESIN COMPOSITION

(71) We, KUREHA KAGAKU KOGYO KABUSHIKI KAISHA, a Japanese company of 8, Nihonbashi Horidome-Cho 1-Chome, Chuo-Ku, Tokyo-To, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to vinylidene fluoride resin compositions which are highly flexible and highly resistant to thermal ageing.

Filaments of vinylidene fluoride resin have heretofore been used mostly for fishing lines. When a filament of vinylidene fluoride is wound on a spool it tends to develop a curl, because the resin has a high Young's modulus and does not straighten out when immersed in water. Therefore attempts have been made to produce a vinylidene fluoride resin filament which is more flexible and which does not so readily curl up as the pure polymer by incorporation thereinto of a plasticiser. Unfortunately conventional plasticisers tend to bleed out and give little benefit as regards the properties of the resin, and especially in the case of filaments this is a serious problem on account of the high surface area to volume ratio of a filament.

Known methods of imparting flexibility to a resin include the addition of a plasticizer which is not a polymer, blending the resin with other polymeric material, preparing the resin in the form of a copolymer with other polymeric material and chemically modifying the resin. Of these, the addition of a plasticizer or the blending of the resin with other polymeric materials probably constitute the most convenient methods of imparting flexibility to a vinylidene fluoride resin, because these methods merely involve blending processes.

Only a few materials, however, are known to be compatible with vinylidene fluoride resin. An example of such a material is polymethyl methacrylate (PMMA). Certain low molecular weight materials which are known to be soluble in vinylidene fluoride resins are phthalic esters such as dimethyl phthalate (DMP) and dibutyl phthalate (DBP). It has been found, however, that mixtures of vinylidene fluoride resin with any of these materials have serious disadvantages. For example, in the case of PMMA, mixing of this with vinylidene fluoride resin does not provide the desired improvement in flexibility, and PMMA is thus useless for this purpose. Again, whilst DMP and DBP can impart a certain degree of flexibility to vinylidene fluoride resin when incorporated therein, each of these materials has a low boiling point at about 300°C. As a result, when a vinylidene fluoride resin, into which an appropriate amount of DMP or DBP has been incorporated, is melt-extruded at a temperature of the order of 300°C, the DMP and DBP vapourize off, and it is therefore impossible to control accurately the amount of these materials which are ultimately found in the extruded product. Furthermore, both DMP and DBP tend to bleed out in a significant amount with the elapse of time after melt-extrusion of the resin. Accordingly, DMP and DBP are not suitable for practical use as plasticisers for imparting flexibility to vinylidene fluoride resins.

Other materials known as plasticizers and which are compatible with vinylidene fluoride resin and are capable of imparting flexibility thereto, are polyesters having a molecular weight of between 1,100 and 5,000, which are obtained from an acid having from 4 to 8 carbon atoms and an alcohol having from 4 to 7 carbon atoms (see for example U.S. Patent No. 3,541,039). However, in

practice these polyesters tend to bleed out in a significant amount with the elapse of time, and are thus unsuitable for the presently described use.

As a result of studies carried out on various other polyesters in seeking to find more effective plasticizers than the aforementioned polyester plasticizers, we have found that, in blending a vinylidene fluoride resin with a polyester, the compatibility of the polyester with the resin depends largely upon the group which is attached at each end of the chain of the polyester. More specifically, we have found out that whilst a commercially available saturated aliphatic polyester can be easily blended with vinylidene fluoride resin by roll kneading and the resulting blend can be conventionally pressed into a transparent sheet, the amount of polyester which bleeds out from the blend with time is largely dependent upon the type of group which is found at each end of the polyester.

The polyesters at present commercially available as high molecular weight plasticizers include polyesters comprising a chain, each end of which terminates in a carboxylic acid group (—COOH) or in an alcoholic hydroxyl group (—OH) or, via an ester linkage in a group derived from a monobasic acid or a monohydric alcohol, each having a relatively high number of carbon atoms ranging from 8 to 12. All these polyesters tend to bleed out in large amounts with the elapse of time and are therefore not very effective from the practical point of view.

The present invention provides a vinylidene fluoride resin composition comprising 100 parts by weight of a vinylidene fluoride resin with from 1 to 10 parts by weight of a polyester comprising a chain which contains recurring units of an ester obtained from a dihydric alcohol having from 2 to 4 carbon atoms and a dicarboxylic acid having from 4 to 6 carbon atoms and having a molecular weight of from 1,500 to 4,000, and each end of the chain of said polyester terminating via an ester linkage, in a group derived from a monobasic acid having from 1 to 3 carbon atoms or monohydric alcohol having from 1 to 3 carbon atoms.

We have found that such polyesters used according to this invention do bleed out from vinylidene fluoride resin compositions but to a much lesser extent than the commercially available polyesters comprising a chain, each end of which terminates in end groups as described previously. The polyesters used according to this invention are thus excellent as plasticizers for vinylidene fluoride resins. We have found also that the compatibility of these polyesters with vinylidene fluoride resin depends upon the number of carbon atoms in the acid and the alcohol from which recurring ester units of the polyester is derived, as well as upon the molecular weight of the polyester. Specifically, where the polyester comprises a chain which contains recurring ester units obtained from a dihydric alcohol having from 2 to 4 carbon atoms and a dicarboxylic acid having from 4 to 6 carbon atoms which has a molecular weight of from 1,500 to 4,000 and each end of the chain of which terminates, via an ester linkage, in a group derived from a monobasic acid or monohydric alcohol, each having from 1 to 3 carbon atoms, the composition undergoes a remarkably small amount of bleeding-out on ageing.

There is a practical difficulty from the point of view of loss of the polyester on ageing, in providing a composition containing more than 10 parts by weight of polyester per 10 PHR with respect to 100 parts by weight of vinylidene fluoride resin. Also, since a composition containing less than 1 part by weight of polyester per 100 parts by weight of resin does not have the characteristic features desired for the product as outlined previously, it is necessary that the quantity of the polyester used in the compositions of the invention be therefore from 1 to 10 parts by weight per 100 parts by weight of vinylidene fluoride resin.

The vinylidene fluoride resin for use in the compositions of the present invention preferably has an inherent viscosity η_i of from 0.7 to 2.0 as measured at a concentration of the resin in a dimethylformamide solution of 0.4 g/dl at a temperature of 30°C. A vinylidene fluoride resin having an inherent viscosity of from 0.8 to 1.8 is particularly preferred for reasons of hot-melting workability, stretching workability, and mechanical strength.

The present invention is further illustrated by the following specific examples of practice thereof.

Example 1.

5 parts by weight of each of various polyesters was blended with 100 parts by weight of a vinylidene fluoride resin having an inherent viscosity of 1.00. The resulting resin compositions were each roll-kneaded at a temperature of 190°C and then pressed at a temperature of 220°C and a pressure of 150 kg/cm² into a sheet 0.5 mm thick. The pressed sheet was interposed between two sheets of

Indian paper, and the resulting sandwich was left in a dry hot atmosphere at 80°C under a load of 0.1 kg/cm^2 for seven days and subsequently examined to determine the quantity of polyester which had bled out. The results are shown in Table 1.

From Table 1, it is apparent that the use of polyesters according to the present invention results in much lower rates of loss of polyester from the resin composition than does the use of commercially available polyesters (which polyesters generally have either end groups containing more than 3 carbon atoms or a molecular weight below 1500), and that the former polyesters are suitable, while the latter polyesters are unsuitable for use as plasticizers in vinylidene fluoride resin compositions.

TABLE 1

	Added polyester	Molecular weight	Amount of bleeding after 7 days (g/m²)
Prior art polyester (Comparative Example)	(1) "ADK cizer P-200"*	2000	4.0
	(2) "AKD cizer PN-280"*	2000	3.3
	(3) "ADK cizer PN-350"*	3000	2.7
	(4) "ADK cizer PN-220"*	–	4.4
	(5) "Diacizer-406"**	–	3.2
	(6) "Diacizer-409"**	–	3.3
	(7) "Polycizer W-300"***	3000	4.0
	(8) $HO\!-\!(PG-AG)_n\!-\!PG-OH$	1400	0.45
	(9) $H\!-\!(AG-PG)_n\!-\!AG-H$	1350	0.95
This Invention	(10) $CH_3-\overset{O}{\overset{\|}{C}}-O\!-\!(PG-AG)_n\!-\!PG-O-\overset{O}{\overset{\|}{C}}-CH_3$	1700	0.20
	(11) $CH_3-\overset{O}{\overset{\|}{C}}-O\!-\!(PG-AG)_n\!-\!PG-O-\overset{O}{\overset{\|}{C}}-CH_3$	2300	0.15
	(12) $CH_3-\overset{O}{\overset{\|}{C}}-O\!-\!(PG-AG)_n\!-\!PG-O-\overset{O}{\overset{\|}{C}}-CH_3$	3000	0.13
	(13) $CH_3-\overset{O}{\overset{\|}{C}}-O\!-\!(Bu-AG)_n\!-\!Bu-O-\overset{O}{\overset{\|}{C}}-CH_3$	1600	0.21
	(14) $H-\overset{O}{\overset{\|}{C}}-O\!-\!(PG-AG)_n\!-\!PG-O-\overset{O}{\overset{\|}{C}}-H$	2100	0.18
	(15) $C_2H_5-\overset{O}{\overset{\|}{C}}-O\!-\!(PG-AG)_n\!-\!PG-O-\overset{O}{\overset{\|}{C}}-C_2H_5$	1800	0.22

PG: Propylene glycol radical Bu: Butanediol radical AG: Adipate radical

The prior art polyesters (1) to (7) all have an end group of an acid or alcohol having from 8 to 12 carbon atoms, and are products manufactured by Adeka Argus Co., Japan (*), by Mitsubishi Monsanto Co., Japan (**), and by Dainippon Ink and Chemical Co., Japan. (***)

It is apparent from Table 3 that the polyester used in accordance with the present invention, even when present in a stretched filament of the resin-polyester composition exhibits good compatibility with the vinylidene fluoride resin, and suffers little ageing degradation. Further, the use of such polyesters as a plasticizer addition gave only a slight reduction in the knot strength which is an important property for a fishing line.

Example 4.

The spun filaments obtained in Example 3 containing 5 parts by weight of polyester were stretched and stored for a period of one month. At the end of this period, each of the stretched filaments was wound in a single ply on a tube having an outer diameter of 30 mm. and the resulting assembly was left in the Gear oven at a temperature of 40°C for 48 hours. The assembly was then removed from the oven and the filament unwound. One end of the unwound filament was lightly clipped at its upper end and freely hung from that end. The filament was then cut in such a manner as to leave hanging a portion measuring 1 metre in length from the clipped point and the vertical distance from the clipped end to the free end of the portion was measured as an indication of the curling property of the filament; it was 72 cm. For a filament containing no polyester the vertical distance was 55 cm.

Another sample was tested for this property of curling under the same conditions except that the polyester used was $H{-}(AG{-}PG)_{\bar{n}}AG{-}H$ as used in Experiment No. 9 of Table 1. The measured distance in this case was 59 cm.

WHAT WE CLAIM IS:—

1. A vinylidene fluoride resin composition comprising a vinylidene fluoride resin and a polyester comprising a chain which contains recurring ester units obtained from a dihydric alcohol having from 2 to 4 carbon atoms and a dicarboxylic acid having from 4 to 6 carbon atoms, said polyester having a molecular weight of from 1,500 to 4,000, and each end of the chain of said polyester terminating, via an ester linkage, in a group derived from a monobasic acid having from 1 to 3 carbon atoms or a monohydric alcohol having from 1 to 3 carbon atoms, the composition containing, per 100 parts by weight of the vinylidene fluoride resin, from 1 to 10 parts by weight of the polyester.

2. A composition according to claim 1, wherein the vinylidene fluoride resin has an inherent viscosity of from 0.7 to 2.0 as measured at a concentration of the resin in a dimethyl-formamide solution of 0.4 g/dl at a temperature of 30°C.

3. A composition according to claim 2, wherein the vinylidene fluoride resin has an inherent viscosity of from 0.8 to 1.8 as measured at a concentration of the resin in a dimethylformamide solution of 0.4 g/dl at a temperature of 30°C.

4. A composition according to any of claims 1 to 3, wherein the polyester is expressed by the formula:

$$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}(PG{-}AG)_{\bar{n}}PG{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$$

wherein PG represents a propylene glycol radical and AG represents an adipate radical, said polyester having a molecular weight of 1,700.

5. A composition according to any of claims 1 to 3, wherein the polyester is expressed by the formula:

$$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}(PG{-}AG)_{\bar{n}}PG{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$$

wherein PG represents a propylene glycol radical and AG represents an adipate radical, said polyester having a molecular weight of 2,300.

6. A composition according to any of claims 1 to 3, wherein the polyester is expressed by the formula:

$$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}(PG{-}AG)_{\bar{n}}PG{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$$

Example 2.

The Young's modulus of elasticity of each of several sheets prepared in Example 1 and of similar sheets which had been subjected to the bleeding test of Example 1 was measured immediately after shaping and after the bleeding test, respectively, according to ASTM, D-638. The results are shown in Table 2.

TABLE 2

Experiment No. of Example 1	Addition quantity (PHR)	Young's modulus of elasticity (kg/mm^2)		Note
		Initial	after 7 days	
(no polyester addition)	0	128	130	Control
No. 9	5	100	115	Control
No. 10	5	98	105	Present invention
No. 11	5	102	104	Present invention
No. 13	5	103	105	Present invention

Example 3.

To 100 parts by weight of a vinylidene fluoride resin having an inherent viscosity of 1.10 was added a polyester which had a molecular weight of 2,300 and which was represented by the formula:

$$CH_3-\overset{\overset{\large O}{\|}}{C}-O\!\left(PG-AG\right)_{\overline{n}}PG-O-\overset{\overset{\large O}{\|}}{C}-CH_3$$

wherein PG represents a propylene glycol and Ag an adipate radical, in quantities as indicated in the following Table 3. Each of the resulting compositions was melt-extruded through an extruder and then stretched at a rate of 5.7 at a temperature of 160°C to produce a filament having a diameter of 250μ (790 denier). Subsequently, the Young's Modulus of elasticity and knot strength of the filament thus obtained were measured immediately after stretching and after further months storage, respectively. The Young's modulus of elasticity and knot strength were measured according to ASTM, D-2256 (the numerical values obtained being calculated in terms of kg/mm^2). The results are shown in Table 3.

TABLE 3

Quantity of polyester used (parts by weight)	Young's modulus of elasticity (kg/mm^2, at 23°C)		Knot strength (kg/mm^2) After storage at 60°C for one month
	Immediately after stretching	After storage at 60°C for one month	
0	270	275	58.0
3	230	235	57.2
5	200	205	56.6
7.5	185	195	56.1
10	160	170	55.3

wherein PG represents a propylene glycol radical and AG represents an adipate radical, said polyester having a molecular weight of 3,000.

7. A composition according to any of claims 1 to 3, wherein the polyester is expressed by the formula:

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O\left(Bu-AG\right)_n Bu-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

wherein Bu represents a butanediol radical and AG represents an adipate radical, said polyester having a molecular weight of 1,600.

8. A composition according to any of claims 1 to 3, wherein the polyester is expressed by the formula:

$$H-\overset{\overset{\displaystyle O}{\|}}{C}-O\left(PG-AG\right)_n PG-O-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

wherein PG represents a propylene glycol radical and AG represents an adipate radical, said polyester having a molecular weight of 2,100.

9. A composition according to any of claims 1 to 3, wherein the polyester is expressed by the formula:

$$C_2H_5-\overset{\overset{\displaystyle O}{\|}}{C}-O\left(PG-AG\right)_n PG-O-\overset{\overset{\displaystyle O}{\|}}{C}-C_2H_5$$

wherein PG represents a propylene glycol radical and AG represents an adipate radical, said polyester having a molecular weight of 1,800.

10. A vinylidene fluoride resin composition according to claim 1 and substantially as herein described with reference to the Examples.

ELKINGTON & FIFE,
Chartered Patent Agents,
High Holborn House,
52/54 High Holborn,
London WC1V 6SH.
Agents for the Applicants.

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